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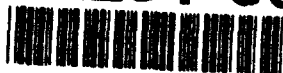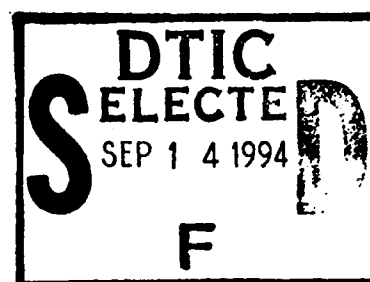
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THE PREPARATION OF ALL para-POLYPHENYLS WITH INCREASED SOLUBILITY AND ENHANCED THIRD ORDER NLO ACTIVITY

Marilyn R. Unroe
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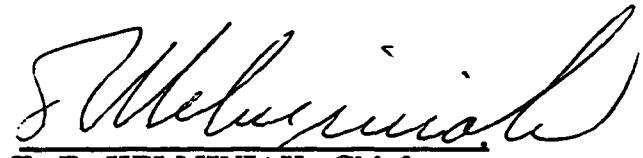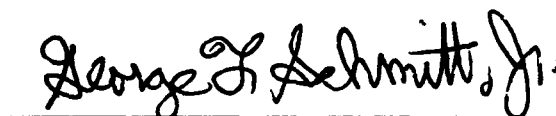
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A series of all para-polyphenyenes up to heptaphenyl were prepared with solubilizing n-decyloxy pendants. The n-alkoxy pendants allow solubility in tetrahydrofuran for evaluation by femtosecond degenerate four-wave mixing. The physical, chemical, and electro-optical measurements are summarized. The oligomers corresponding to monomer and trimer have increased second hyperpolarizability due to purely extended π–conjugation effects. However, the pentamer and heptamer evaluations indicated large increases in hyperpolarizability which were not solely attributable to conjugation increases. Furthermore, two-photon resonance enhancement was confirmed in the heptamer by an upconverted blue emission of the heptamer solution at 602nm. Two photon resonance was suspected in the pentamer because of less intense blue emission.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Dir~~ . ~ ~e Wright Laboratory, Air Force Materiel Command, Wright-Patterson Air Force Base, Ohio with Dr. Robert C. Evers as the Materials Laboratory Project Scientist. Coauthors were Marilyn R. Unroe and Bruce A. Reinhardt, Materials Directorate (WL/MLBP). This report covers research conducted from February 1989 to September 1989. The authors wish to thank personnel of the Materials Integrity Branch, WL/MLSA, Systems Support Division, Materials Directorate, for mass spectrum and elemental analysis determinations; Ann Dombroskie, University of Dayton Research Institute, and Martin M. Wright and Paul Roderer, Southwestern Ohio Council for Higher Education, Student Support Program, for synthesis support. The authors also wish to acknowledge the personnel of the Photonics Research Laboratory, State University of New York at Buffalo, and especially Dr. Paras Prasad, for performance of the degenerate four-wave experiments.

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SECTION 1. INTRODUCTION

Many of the recent developments in the area of third order nonlinear optical materials have concerned the structure-property relationships associated with the third order nonlinear response. While the preparation of molecules which exhibit only nonresonant electronic nonlinear response are desired for optical waveguide devices, there have been an increasing number of molecules prepared which exhibit higher third order responses due to two photon resonance absorption phenomena (References 1-3). A high nonresonant response for the bulk susceptibility, $\chi^{(3)}$, is required for a waveguiding device since no losses of intensity via absorption of any kind can be tolerated. The presence of two photon absorption is characterized by two experimental observations: first, the actual value of $\chi^{(3)}$ is enhanced by the presence of a large imaginary component to the molecular second hyperpolarizability, γ. Secondly, the effective nonlinearity in a degenerate four wave mixing (DFWM) experiment is skewed due to the additive effect of the enhanced $\chi^{(3)}$ in the appropriate equation. Thus, large but resonance enhanced values of $\chi^{(3)}$ are obtained for materials that exhibit two photon absorption. In a recent publication (Reference 4) the increase in π conjugation length by increasing the moleular weight of a series of substituted all para-polyphenyls was explored using DFWM techniques. The conclusions of this publication verified that as π conjugation length increases from the monomer to the trimer, there is a concurrent linear increase in γ. However, no values for unsubstituted polyphenyls beyond the trimer unit were available due to lack of solubility of the oligomers to be measured. In other reports on a series of polyenes and polyvinylenes (Reference 5), a response maximum for γ was obtained beyond which it was purported that there was no significant increase in γ. The ultimate problem with extrapolating legitimate hypotheses from all the previous research has been a chronic problem known to polymer chemists for years: how to increase molecular weight while maintaining solubility of the intermediates and products in the reaction media or in the solvent for evaluation. It is to this purpose that

a series of all para-polyphenyls containing pendant long chain alkoxy groups was prepaied and was evaluated in dilute tetrahydrofuran (THF) solutions by DFWM . The following report details the synthesis and DFWM results of the soluble polyphenyls.

SECTION 2. RESULTS AND DISCUSSION

2.1. Synthetic Preparations

The decyloxy ($-OC_{10}H_{21}$) substituted para-polyphenyl oligomers corresponding to monomer, trimer, pentamer, and heptamer were synthesized for measurement by DFWM. The monomer, 1, 4-bis(decyloxy)benzene, was synthesized in 84% yield by a procedure similar to that described in the literature for the synthesis of aromatic diethers (Reference 6) (Figure 1).
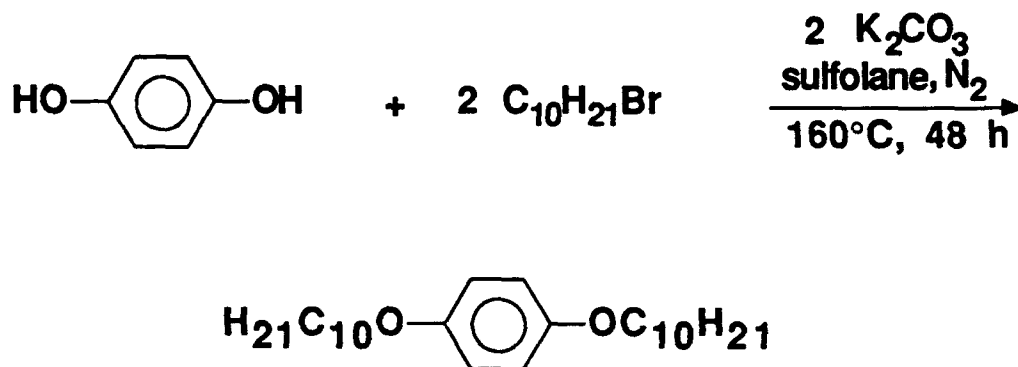
Figure 1. Synthesis of 1,4-Bis(decyloxy)benzene (Monomer).

Trimer (n = 0), pentamer (n = 1), and heptamer (n = 2) were synthesized in yields of 43, 41, and 15% respectively by a synthetic scheme previously developed in this laboratory (Reference 7) for the synthesis of unsubstituted and phenyl substituted para-polyphenyls (Figure 2).
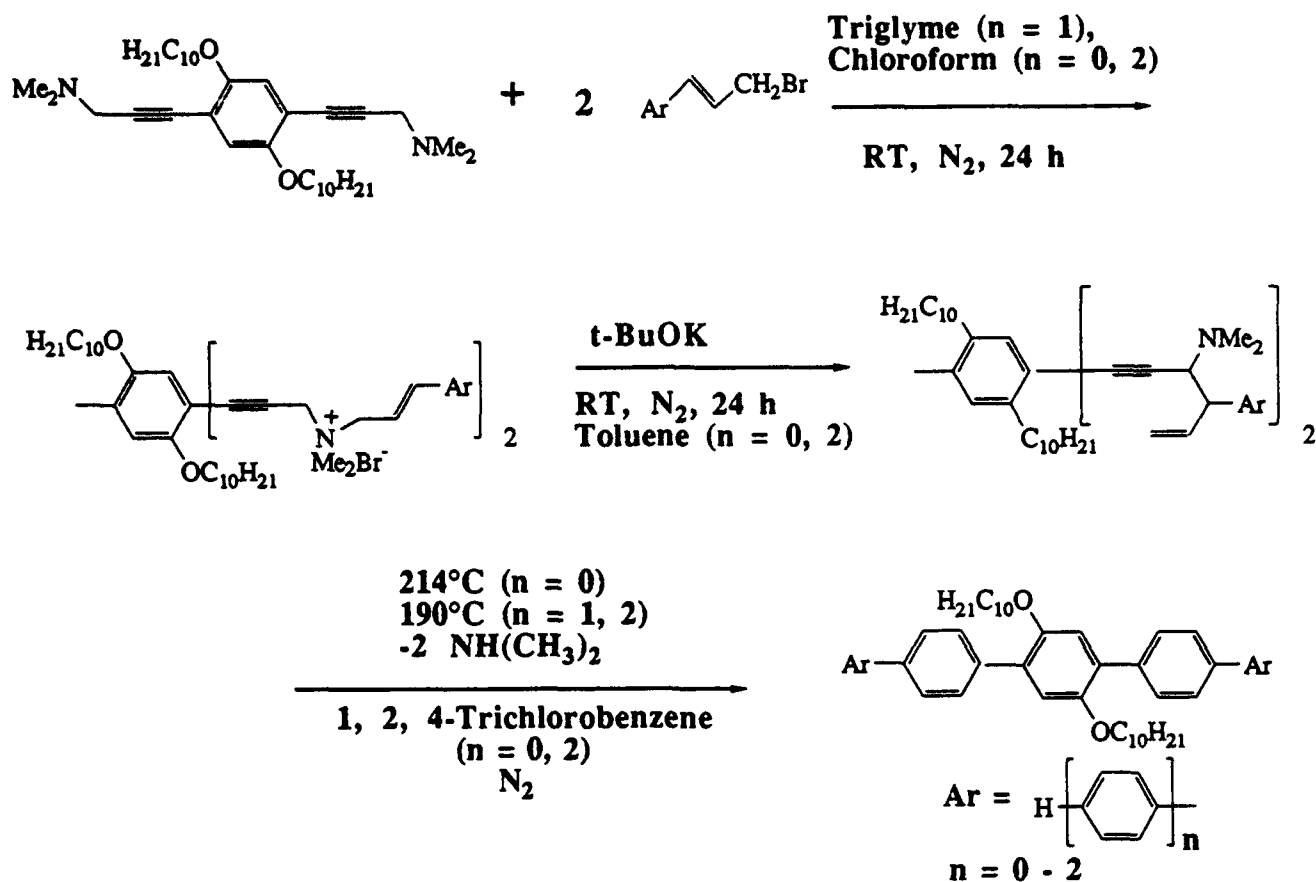
Figure 2. Synthetic Scheme For Decyloxy Substituted para-Polyphenyl Trimer (n = 0), Pentamer (n = 1), and Heptamer (n = 2).

Although the trimer, pentamer, and heptamer were prepared by one-pot procedures, isolation of the trimer and heptamer intermediates at each step of the synthesis was found to increase the overall yield. The advantage of utilizing such a preparatory scheme was the complete isolation of the all para- isomer from its ortho-ortho- and ortho-para- isomers during thermal closure to the final polyphenyl (References 8, 9).

The physical characterization of the decyloxy substituted polyphenyls is summarized in Table 1. Typically the yield decreased as the length of the polyphenyl chain increased; this loss of yield was also observed to occur during the preparation of the

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Table 1. Physical Characterization of Decyloxy Substituted Polyphenyls.

X MER	YIELD (%)[a]	MELTING POINT (°C)	APPEARANCE (SOLVENT)	SOL. AT 25°C	FORMULA (FW)	ELEM. ANAL. CALC. (FOUND)	E.I.M.S m/z (%)[b]
Monomer	84	68[c] Lit mp 68[d]	colorless plates (MeOH)	CHCl$_3$ THF	C$_{26}$H$_{46}$O$_2$ (390.62)	C, 79.94 (79.92) H, 11.87 (11.85)	390 (25, M$^+$) 110 (100)
Trimer (n = 0)	43	65.8-67.1[e]	white pwd. (EtOH)	CHCl$_3$ THF	C$_{38}$H$_{54}$O$_2$ (542.81)	C, 84.08 (84.38) H, 10.03 (9.86)	542 (13, M$^+$) 43 (100)
Pentamer (n = 1)	41	123-126[c]	yel. needles (2-propanol)	CHCl$_3$ heptane THF	C$_{50}$H$_{62}$O$_2$ (694.99)	C, 86.40 (86.70) H, 8.98 (9.00)	695 (19, M$^+$) 43 (100)
Heptamer (n = 2)	15	185-187[c]	yel. needles (cyclohexane)	THF	C$_{62}$H$_{70}$O$_2$ (847.17)	C, 87.89 (87.77) H, 8.33 (8.35)	847 (1, M$^+$) 43 (100)

[a] Purified yield.

[b] Emission ionization mass spectra performed t$_y$ WL/MLSA, Wright-Patterson AFB, OH.

[c] Uncorrected.

[d] Reference 10.

[e] Corrected melting point from Mel-Temp II apparatus with a calibrated Fluke Model 51 thermocouple.

previously reported polyphenyls prepared by such a route (Reference 7). Melting points of the polyphenyls increased as molecular weight increased. In addition, higher boiling, more nonpolar solvents were required for recrystallization as the molecular weight of the polyphenyl increased. All polyphenyls were soluble in tetrahydrofuran at room temperature and thus provided a means to prepare dilute solutions of the polyphenyls for DWFM experiments.

2.2 Summary of DFWM Experiments

The measurements of the third-order NLO activity were performed using femtosecond DFWM in varying concentrations of dilute THF solutions as low as 0.001 M. These data are summarized in Table 2 together with the ultraviolet/visible (UV/VIS) spectra of the oligomers. The advantages of using dilute solutions versus the film technique for

Table 2. Nonlinear Optical Measurements For Didecyloxy Substituted n-Polyphenyls (Reference 3).

	Monomer	Trimer	Pentamer	Heptamer
λ (nm) [a]	291.9	318.9	331.4	335.8
v [b] X 10^{-4} (cm^{-1})	3.426	3.136	3.018	2.978
ε [c] (l $mol^{-1}cm^{-1}$)	2800	12300	31900	32000
λ (nm) [d]	238.2	266.1	289.6	299.6
v X 10^{-4} (cm^{-1})	4.198	3.758	3.453	3.338
ε (l $mol^{-1}cm^{-1}$)	3200	21000	32000	42000
γ (esu) [e]	2.2 X 10^{-35}	6.9 X 10^{-35}	3.5 X 10^{-34}	-3.3 X 10^{-33} (r) 7.2 X 10^{-33} (im)

[a] Peak absorption wavelength refers to the lowest energy transition for the monomer through the heptamer.
[b] Bandgap.
[c] Linear absorbance coefficient.
[d] Peak absorption wavelength refers to the second lowest energy transition for the monomer through the heptamer.
[e] Orientationally averaged scalar part of the third-order hyperpolarizability.

third-order NLO measurements by DFWM include the avoidance of occlusions and nonuniformities in films which skew the calculation of γ from the experimental data.

During exposure to the 602 nm laser beam the heptamer solutions exhibited a strong visible blue fluorescence. This upconverted blue emission is due to the two-photon absorbance of the heptamer and is very visible even at the lowest concentrations. The pentamer also exhibited blue fluorescence although weaker than the heptamer at equivalent concentrations. No visible fluorescence was observed for the monomer and trimer. The presence of two-photon absorption is further clarified in the temporal profiles of the trimer and heptamer solutions which demonstrate time dependent response population gratings of

the excited species (Figures 3 and 4). The profile of the trimer in Figure 3 exhibits
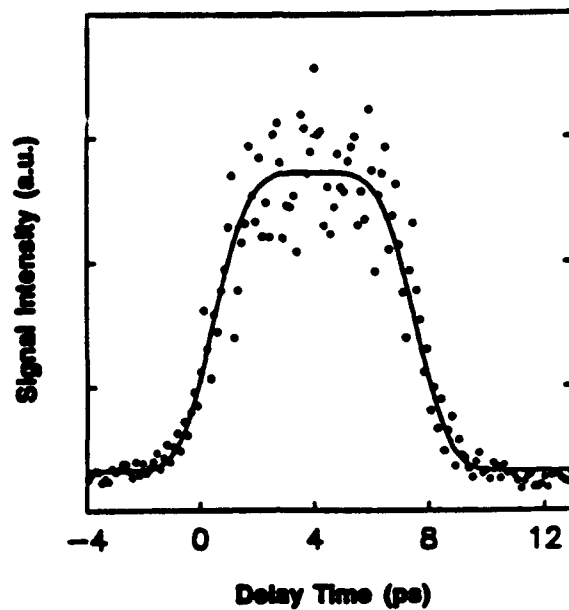

Figure 3. Temporal DFWM Profile For Trimer Solution Obtained by Delaying Beam 2. Solid Curve is Theoretical Fit (Reference 3).
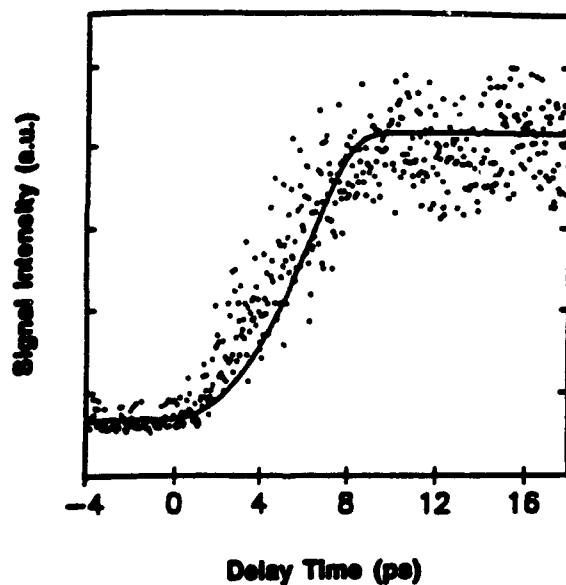

Figure 4. Temporal DFWM Profile For Heptamer Solution Obtained by Delaying Beam 2. Solid Curve is Theoretical Fit (Reference 3).

the anticipated Gaussian distribution of a nonresonant enhanced NLO material and is flattened at the peak of the curve because the pulse width of the laser is shorter than the sample thickness of 1 mm in the cuvette. With a laser pulse width of 500 femtoseconds, the spatial overlap length of the two counterpropagating laser pulses is about 0.15 mm. The width of the plateau can be minimized by obtaining a closer match of sample thickness with the overlap length of the lasers. The s-curve profile of the heptamer in Figure 4 indicates the contribution of two-photon resonance enhancement to the experimental values plotted. The upper portion of the curve in Figure 4 is indicative of a long decay rate for the DFWM signal and such a decay rate is dominated by a population grating whose effective γ value is complex at 602 nm. A complex value is defined for these purposes as contributions from refractive index and the absorption coefficient to the parameters which determine the hyperpolarizability, γ. These contributions help to explain the domination of the imaginary component for the heptamer in the four-wave mixing process (Table 2) and the concomitant skewing of Figure 4 from the Gaussian distribution. An additional piece of evidence indicates the contribution of two-photon absorbance in the heptamer: when the power dependence of the backward probe beam of the heptamer is examined as a log-log plot at various concentrations (Reference 3), the influence of the complex population gratings of the heptamer causes a significant slope deviation of the experimental plot from the theoretical plot. This slope deviation is not observed for the monomer and trimer which are not two-photon resonance enhanced and is only inferred to occur slightly for the pentamer. Thus the γ values for the pentamer and heptamer are only effective γ values.

Some conclusions from this study are listed below:

(1) For the decyloxy substituted polyphenyls studied, the third order nonlinearity values increase as molecular weight increases. The γ increase from monomer to trimer is expected from pure π conjugation length increases with no two-photon resonance contributions. The influence of two-photon absorbance induced changes to the refractive index and absorption coefficient parameters which determine γ for the pentamer and

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heptamer result in complex values for the pentamer and heptamer at 602 nm. The γ values obtained, therefore, are only effective γ values for the pentamer and heptamer.

(2) Two-photon resonance enhancement exhibits itself in DFWM as both real and imaginary components to the effective nonlinearity which contribute to the calculation of the bulk susceptibility, $\chi^{(3)}$, and as a bright blue upconverted emission from the THF solution when pulsed at 602 nm. Although a real and imaginary component of γ definitely exist for the heptamer, it is suspected that there is a small but undiscernable imaginary component for γ in the pentamer also. This suspicion for the pentamer is suggested by the log-log plot of the intensity of the backward probe beam at various concentrations of the pentamer and a slight blue emission of the pentamer solutions upon exposure to the DFWM experimental conditions.

(3) Pure samples of the p-polyphenyls with decyloxy pendants were obtained by modification of previously reported procedures. The presence of the alkoxy pendant groups provided solubility of the polyphenyls in THF, a solvent of choice for DFWM experiments.

SECTION 3. EXPERIMENTAL

3.1 Synthetic Procedures

All reagents were used as received from the specified vendors. Solvents were used as received or dried over 4Å molecular sieves before use. All melting points were determined on a Mel-Temp II melting point apparatus as uncorrected values unless otherwise stated. Fourier transform infrared (FTIR) spectroscopy was performed on a Beckman 1000 spectrometer using anhydrous potassium bromide pellets. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were performed on a Varian EM-360A spectrometer using 10% weight/volume concentrations with tetramethylsiloxane (TMS) as standard in deuterated chloroform.

3.1.1. Synthesis of 1,4-Bis(decyloxy)benzene (Monomer)

A mixture of hydroquinone (10.0 g, 0.09 mol), 1-bromodecane (Aldrich, 40.2 g, 0.18 mol), and sulfolane (70 mL) was charged into a 500 mL three-neck roundbottom flask fitted with a nitrogen purge, thermometer and reflux condenser. The mixture was stirred under a nitrogen atmosphere for 0.5 h at room temperature before the addition of potassium carbonate (26.4 g, 0.19 mol) to the flask. The solution was heated by oil bath to an internal temperature of 160°C for 48 h. An aliquot of the solution was quenched in water and thin layer chromatography (TLC) on a silica gel strip (3:1 hexane:methylene chloride eluent) indicated no starting hydroquinone remained. The warm dark brown solution was poured into ice water (1500 mL) to precipitate a tan solid. The solid was collected on a Buchner funnel, air dried, and recrystallized twice from boiling methanol (650 mL each) to give colorless plates (24.39 g, 74%): mp 68°C.

3.1.2. Two-Step Preparation of 2,5-Didecyloxy-1,4-bis(3-dimethylamino-1-propynyl)benzene

To a 2000 mL three-necked roundbottom flask fitted with a mechanical stirrer, thermometer, and reflux condenser was added a suspension of 1,4-bis(decyloxy)benzene (20.0 g, 0.05 mol) in a 10:1:1 solution of acetic acid:sulfuric acid:water (840 mL). After

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the diether was dissolved, iodine (Allied Chemical, 19.5 g, 0.08 mol) and periodic acid (Aldrich, 3.7 g, 0.02 mol) were added to the flask. The solution was heated by oil bath to an internal temperature of 80°C for 1.5 h at which time TLC on a silica gel strip (3:1 petroleum ether: methylene chloride) indicated the reaction was completed. To TLC the reaction, an aliquot was removed from the flask and quenched in saturated sodium bisulfite solution. The solution was then extracted with methylene chloride to remove the organic components. The flask was allowed to cool to room temperature and the solution was poured slowly into aqueous 10% sodium bisulfite (1500 mL) to avoid rapid release of sulfur dioxide. The crude product was precipitated from solution, collected on a Buchner funnel and air dried. After two recrystallizations from 2-propanol (700 mL each) a white cottony solid was obtained (25.2 g, 77%): mp 62°C. FTIR (KBr): $\nu = 2925$, 2850 (s, alkyl C-H), 1475 (s, arom C=C), 1260 (s, assym C-O-C), 1020 cm^{-1}(s, sym C-O-C) (Figure 5).
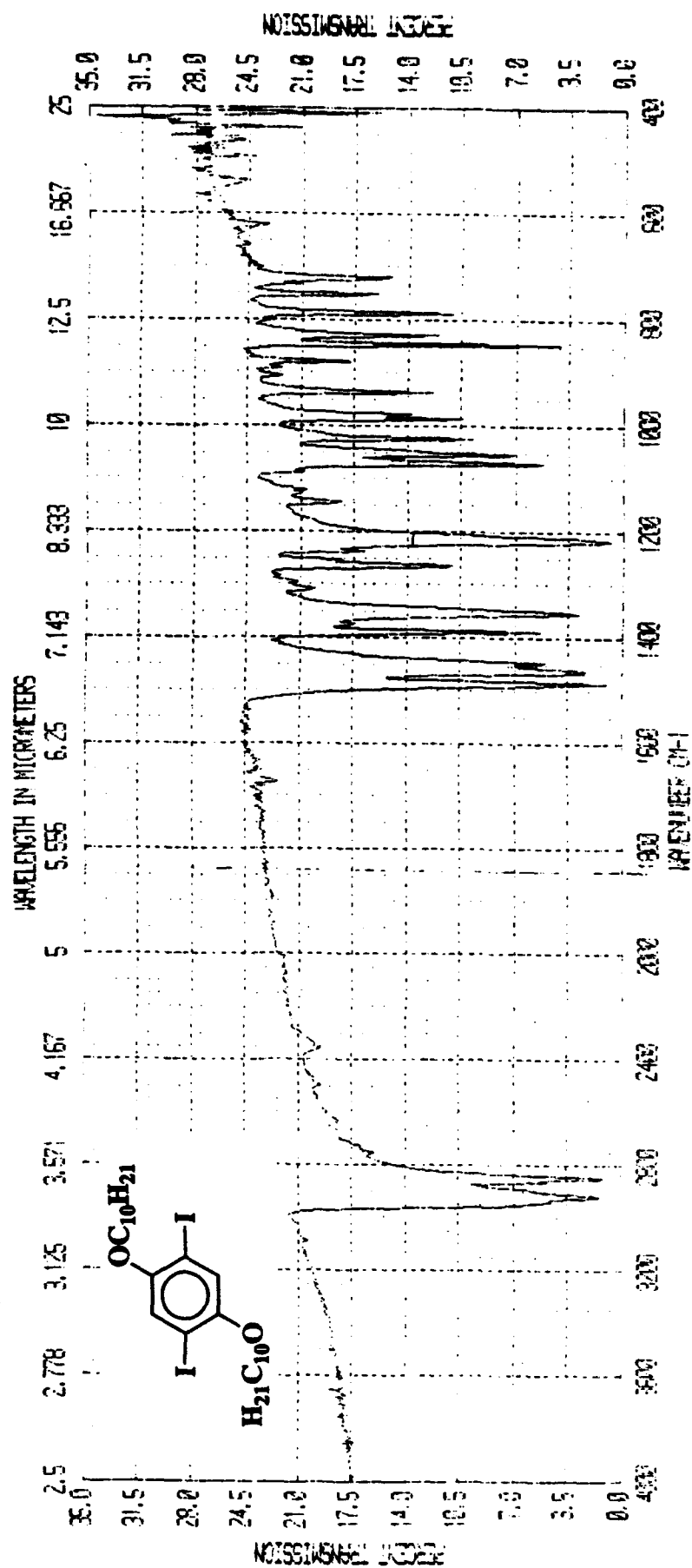
Figure 5. FTIR Spectrum of 2,5-Didecyloxy-1,4-diiodobenzene.

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A solution of 2,5-didecyloxy-1,4-diiodobenzene (10.00 g, 0.02 mol), N, N-dimethylamino-2-propyne (Aldrich, 3.20 g, 0.04 mol), and piperidine (200 mL) was stirred at room temperature under a nitrogen atmosphere for 0.5 h before the addition of cuprous iodide (Alfa, 0.10 g, 0.001 mol) and dichlorobis(triphenylphosphine) palladium (II) (Strem, 0.10 g, 0.001 mol). The flask was heated to an internal temperature of 60°C under nitrogen for 24 h at which time TLC on an alumina gel strip (4:1 methylene chloride:diethyl ether) indicated the reaction was completed. The flask was allowed to cool to room temperature, the salts were filtered from the mixture on a Buchner funnel, and the filtrate was washed with water and separated. The filtrate was acidified to pH = 1 by addition of 20% aqueous hydrochloric acid. The filtrate was then brought to a pH = 8 by the addition of 10% sodium bicarbonate (500 mL). The aqueous layer was separated from the organic layer and the aqueous layer was extracted twice with methylene chloride (250 mL portions) to remove any trapped product. The organic layers were combined and were washed with water (1000 mL), separated, and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo* to afford 7.72 g of crude product. The crude material was filtered over a bed of alumina packed in a Buchner funnel with methylene chloride eluent and the solvent was distilled from the filtrate. The residue was recrystallized from cyclohexane (100 mL) which was cooled below room temperature in the refrigerator to give a yellow-tan powder (4.46 g, 52%): mp 72-74°C. Elem. Anal. calc'd for $C_{36}H_{60}N_2O_2$: C, 78.21; H, 10.94; N, 5.07. Found: C, 78.31; H, 10.82; N, 5.12. Mass spectrum (EIMS): m/z = 553 (16, M+1), 552 (21, M$^+$), 58 (90, $(CH_2=N(CH_3)_2)^+$). ^{1}H-NMR (10%, CDCl$_3$): δ = 6.8 (s, 2H$_{arom}$), 3.9 (t, 4H $_{-O-CH_2-}$), 3.5 (s, 4H $_{C-CH_2-NR_2}$), 2.3 (s, 12H $_{-N-(CH_3)_2}$), 2.2 - 0.5 (m, 38H$_{alkyl}$) (Figure 6). FTIR (KBr): ν = 2950, 2925, 2850, 2825, 2780 (broad, alkyl C-H), 1515, 1470 (m, arom C=C), 1220 (s, assym C-O-C), 1020 cm^{-1}(w, sym C-O-C) (Figure 7).
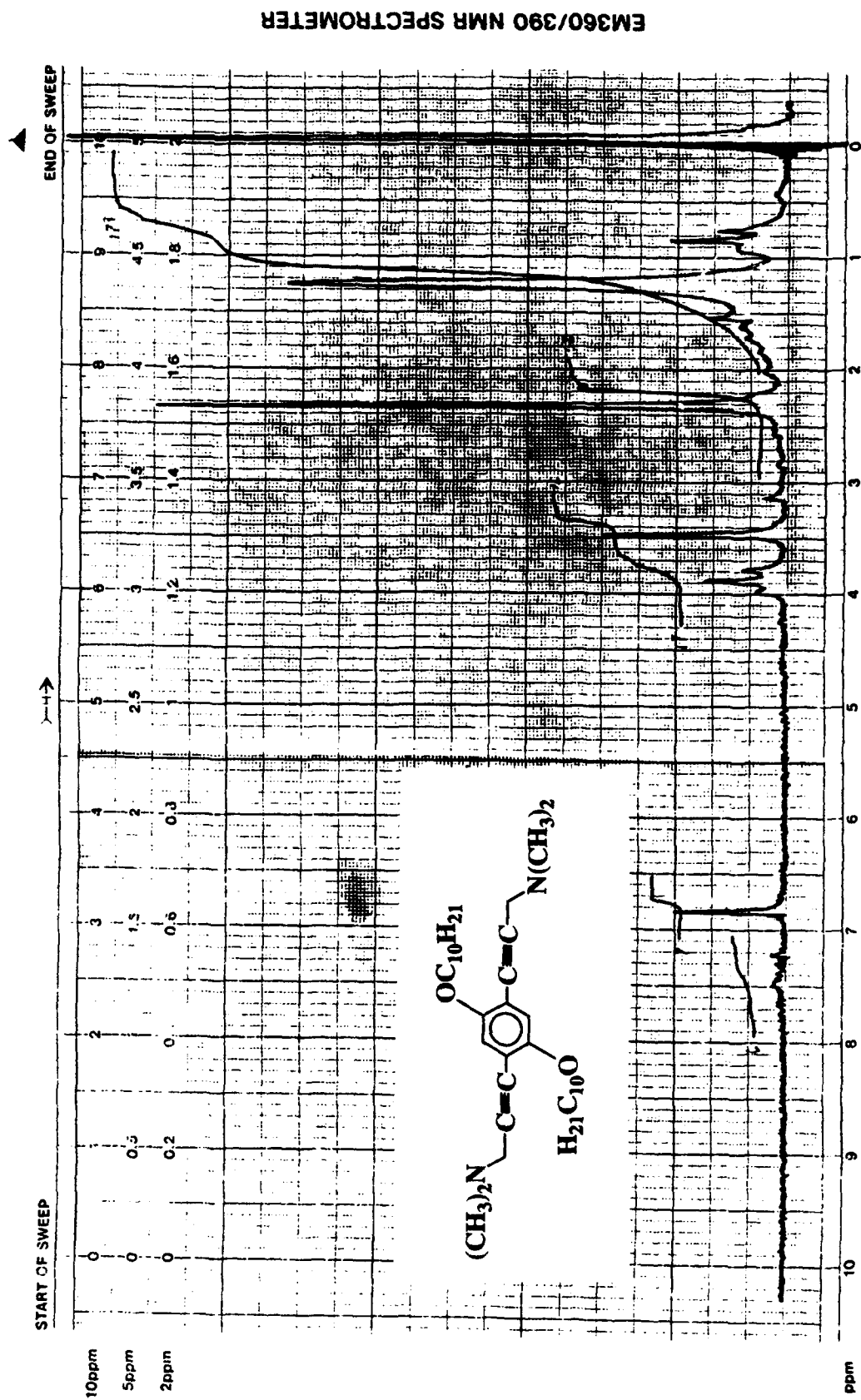
Figure 6. ^{1}H-NMR Spectrum of 2,5-Didecyloxy-1,4-bis(3-dimethylamino-1-propynyl)benzene.
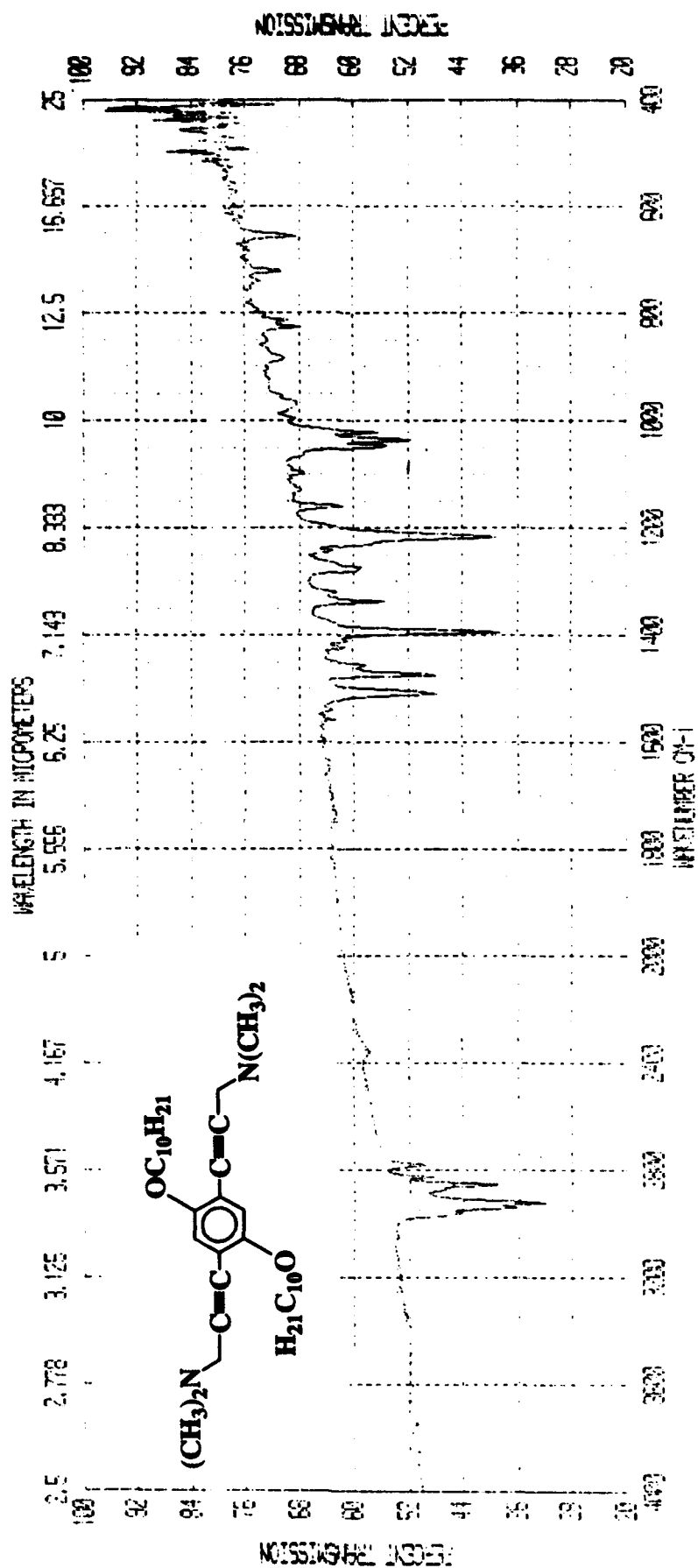
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Figure 7. FTIR Spectrum of 2,5-Didecyloxy-1,4-bis(3-dimethylamino-1-propynyl)benzene.

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3.1.3. (E)-3-Bromo-1-propenylbenzene

This compound was commercially available from Aldrich Chemical Co. and was used as received from the vendor.

3.1.4. Three Step Preparation of (E)-4-(3-Bromo-1-propenyl)biphenyl (Reference 7)

3.1.4.1. Preparation of (E)-3-(4-Biphenylyl)-2-propenal

A solution of 4-iodobiphenyl (6.2 g, 0.02 mol), acrolein (Aldrich, 2.5 g, 0.04 mol), tetra-n-butylammonium chloride (Lancaster, 7.2 g, 0.03 mol), sodium bicarbonate (MCB, 4.6 g, 0.06 mol) and dry N,N-dimethylformamide (75 mL) was stirred by mechanical stirrer for 0.25 h under a nitrogen atmosphere before the addition of fresh palladium diacetate (Strem, 1.2 g, 0.01 mol). The solution was stirred at room temperature under nitrogen for 24 h at which time TLC on a reverse phase plate (80% aqueous ethanol) indicated that no starting material remained. The crude product was isolated by precipitation of the black reaction mixture into water (350 mL) The precipitate was dissolved into hot heptane (300 mL) and cooled to produce pale yellow prisms (2.07 g, 56%): mp 119-120°C (Reference 7, mp 110-112°C).

3.1.4.2. Preparation of (E)-3-(4-Biphenylyl)-2-propen-1-ol

To a 100 mL three-necked roundbottom flask fitted with a drying tube was added a solution of (E)-3-(4-biphenylyl)-2-propenal (2.00 g, 0.01 mol), sodium borohydride (Aldrich, 0.18 g, 0.004 mol), and absolute ethanol (20 mL). The solution was stirred at room temperature under anhydrous conditions until TLC (reverse phase; 80% aqueous ethanol) at t = 96 h indicated that the reaction was complete. To TLC, an aliquot was quenched in water and extracted with diethyl ether and then compared with a starting materials standard. The crude product was precipitated from the reaction mixture by slow

pouring into water (150 mL). After recrystallization from a hot 2-propanol:water mixture (3:1, 200 mL), a white powder was afforded (1.37 g, 67%): mp 160-162°C. FTIR (KBr): v= 3300 (broad OH), 3050, 3000 (w, arom and vinyl C-H), 2905, 2850 (w, methylene C-H), 1580 (s, arom C=C), 1405 cm^{-1}(s, vinyl C-H scissor) (Figure 8).
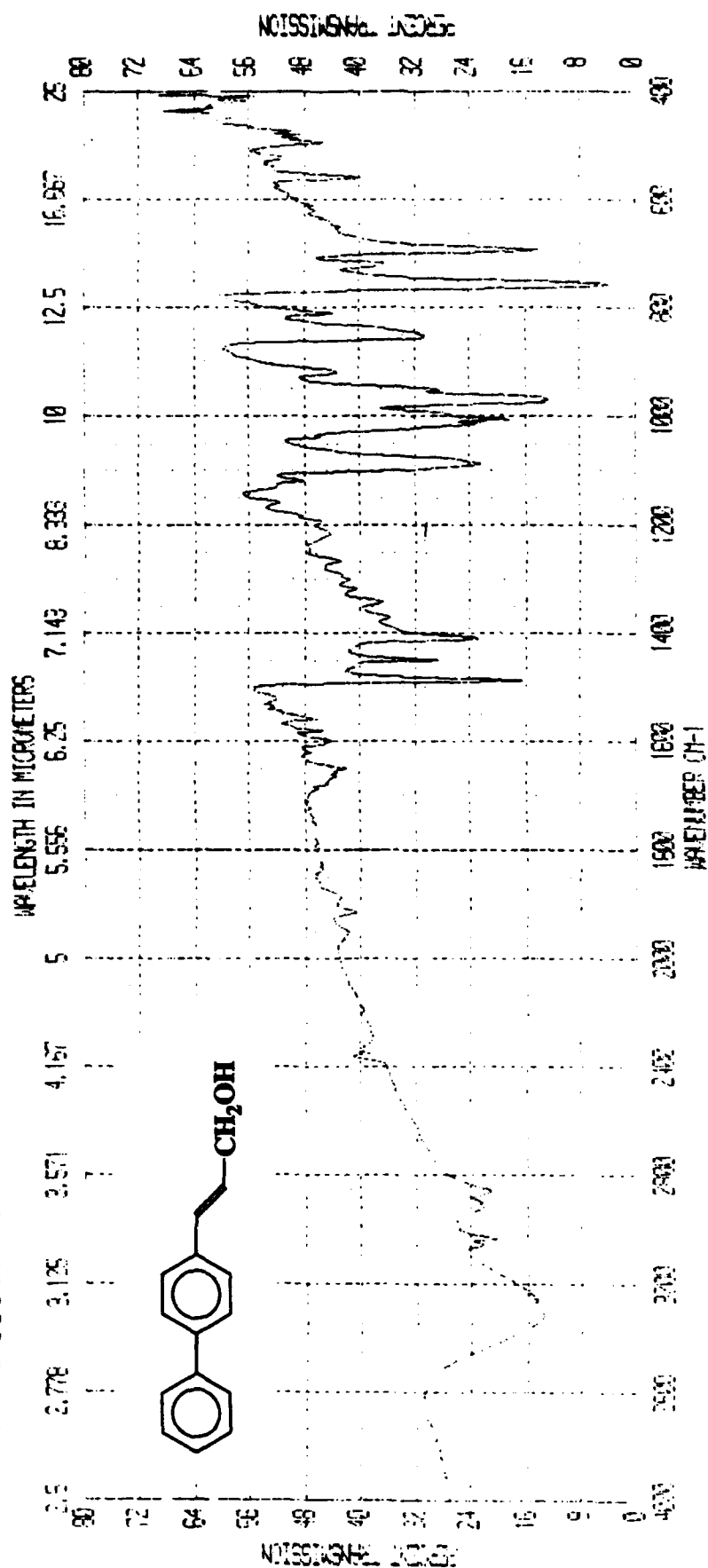
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Figure 8. FTIR Spectrum of (*E*)-3-(4-Biphenylyl)-2-propen-1-ol.

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3.1.4.3. Preparation of (E)-4-(3-Bromo-1-propenyl)biphenyl

To a 250 mL three-necked roundbottom flask fitted with a mechanical stirrer, thermometer, and drying tube was added a solution of (E)-3-(4-biphenylyl)-2-propen-1-ol (2.00 g, 0.01 mol) in diethyl ether (100 mL). The flask was cooled to an internal temperature of 5°C and a solution of phosphorus tribromide (Aldrich, 1.72 g, 0.01 mol) in diethyl ether (25 mL) was added dropwise to the flask over a period of 15 min. The flask was allowed to warm to room temperature and the solution was stirred for a total of 24 h. TLC on a reverse phase plate (80% aqueous ethanol) at t = 24 h indicated the reaction was completed. The crude product was isolated by precipitation of the reaction mixture into water (400 mL) and by collection and drying of the precipitate on a Buchner funnel. The crude product was recrystallized from boiling hexane (50 mL) to afford a pale yellow powder (2.41 g, 93%): mp 135°C. FTIR (KBr): v = 3050, 3000 (w, arom and vinyl C-H), 1475 (s, arom C=C), 1410 cm^{-1} (m, vinyl C-H scissor) (Figure 9).
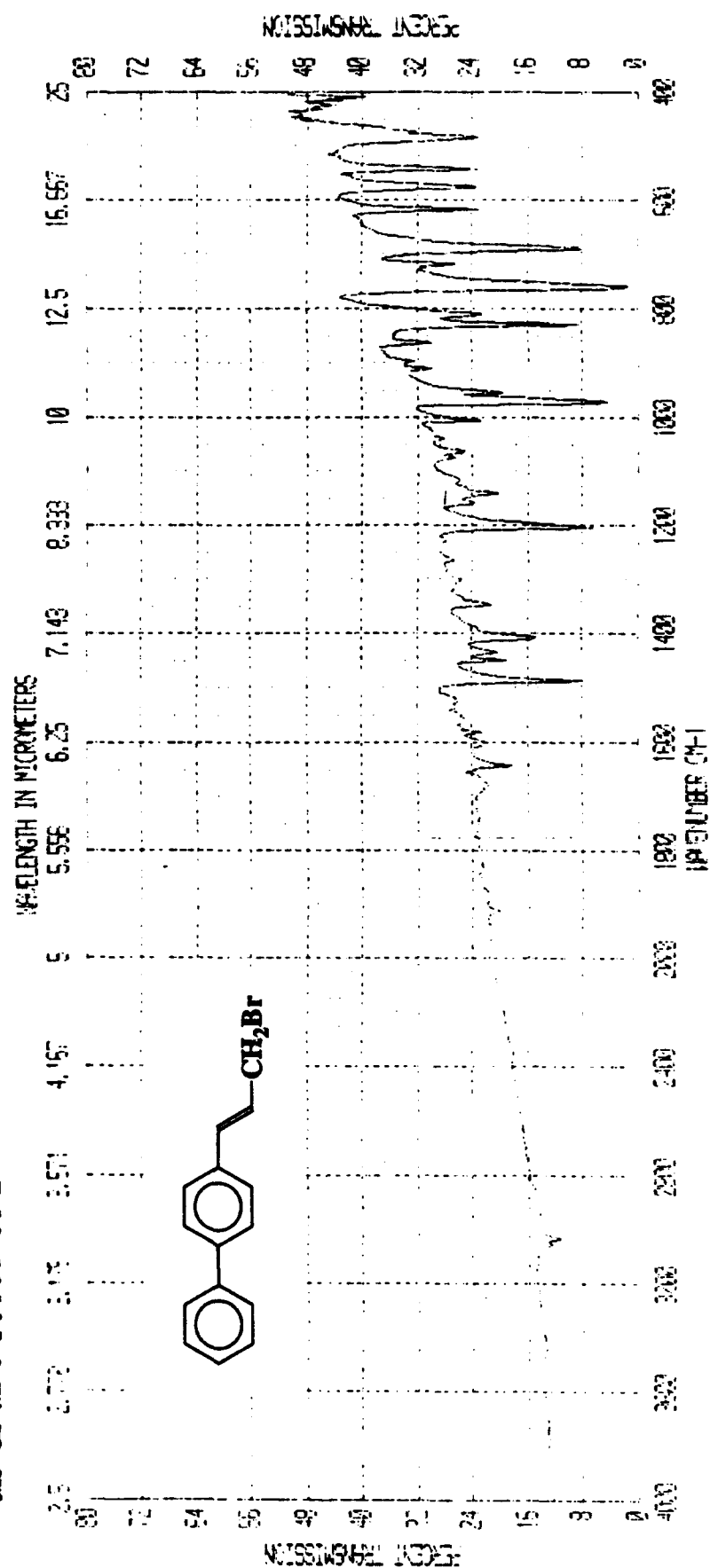
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Figure 9. FTIR Spectrum of (*E*)-4-(3-Bromo-1-propenyl)biphenyl.

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3.1.5. Three-Step Preparation of Trimer

To a 500 mL three-necked roundbottom flask fitted with a drying tube and addition funnel was added a solution of 2,5-didecyloxy-1,4-bis(3-dimethylamino-1-propynyl)-benzene (11.06 g, 0.02 mol) in dry chloroform (200 mL). To the flask was dropwise added a solution of allyl bromide (Aldrich, 5.08 g, 0.04 mol) in dry chloroform (100 mL) at room temperature. The reaction was allowed to stir at room temperature overnight although TLC at t = 2 h showed that the reaction was completed. The solvent was removed *in vacuo* and reagent grade acetone (100 mL) was added to the residue to precipitate a white solid. The solid was filtered from solution and air dried at room temperature under reduced pressure to afford a white solid bisammonium bromide imtermediate (15.09 g, 95%).

The salt intermediate (15.09 g, 0.02 mol) was then suspended in dry toluene (200 mL) in a 500 mL three-necked roundbottom flask while nitrogen gas was bubbled through the suspension for 0.25 h. The bubbler was replaced with a nitrogen blanket and potassium *t*-butoxide (Aldrich, 4.83 g, 0.04 mol) was added incrementally to the flask over a period of 15 min. The suspension was stirred at room temperature under nitrogen for 19 h at which time TLC on a reverse phase plate (acetone) indicated no starting material remained. The toluene was evaporated at room temperature from the solution and the solid residue was stirred with cold pentane to afford a yellow tan solid (9.58 g, 80%).

The bisamine intermediate (9.54 g) was dissolved into 1,2,4-trichlorobenzene (10 mL) in a 100 mL three-necked roundbottom flask fitted with reflux condenser and a gas inlet connected to a Firestone valve. The flask was purged under a nitrogen blanket and refluxed at 214°C for 24 h. The reaction mixture was then allowed to cool to room temperature to precipitate the crude solid polyphenyl. The solid was purified by column chromatography on an alumina gel column using 3:1 chloroform:petroleum ether as the eluent. Subsequent recrystallization from hot ethanol afforded a white solid (4.66 g, 57%; 43% overall yield): mp 65.8-67.1°C (corrected). Elemental analysis and mass spectral data are listed in Table 1.

3.1.6. One-Pot Preparation of the Pentamer

In a 250 mL three-necked roundbottom flask fitted with reflux condenser and gas inlet connected to a Firestone valve were added 2,5-didecyloxy-1,4-bis(3-dimethylamino-1-propynyl)benzene (5.56 g, 0.01 mol), (E)-3-bromo-1-propenylbenzene (4.01 g, mol) and triglyme (100 mL). The solution was stirred under a nitrogen atmosphere for 24 h at room temperature to form the bisammonium bromide intermediate. After 24 h potassium t-butoxide (g, mol) was added to the flask and the solution was stirred for an additional 24 h at room temperature under a nitrogen atmosphere to form the bisamine isomeric mixture. The flask was subsequently heated by oil bath to an external temperature of 190°C under a nitrogen atmosphere for 24 h to complete the Stevens rearrangement to the isomeric polyphenyl mixture. The flask was allowed to cool to room temperature and the solution was filtered over a Buchner funnel to collect the insoluble all para-polyphenyl crude product. The solid was purified by column chromatography through a silica gel column using 1:1 petroleum ether:methylene chloride as the eluent. The eluate was concentrated by distillation of the solvent *in vacuo* on a rotary evaporator to obtain an amorphous light yellow solid. The solid was recrystallized from boiling 2-propanol (450 mL) to afford light yellow needles (2.74 g, 41%): mp 124-127°C. Elemental analysis and mass spectral data are listed in Table 1. ^{1}H-NMR (10%, CDCl$_3$): δ = 8.5 - 6.8 (m, 20H$_{arom}$), 3.9 (t, 4H $_{-O-}$ $_{CH_2-}$), 2.2 - 0.4 (m, 38H$_{alkyl}$) (Figure 10). FTIR (KBr): ν = 3050, 3025 (w, arom C-H), 2930, 2850 (s, alkyl C-H), 1480 (m, arom C=C), 1215 (m, assym C-O-C), 1010 cm^{-1} (w, sym C-O-C) (Figure 11).
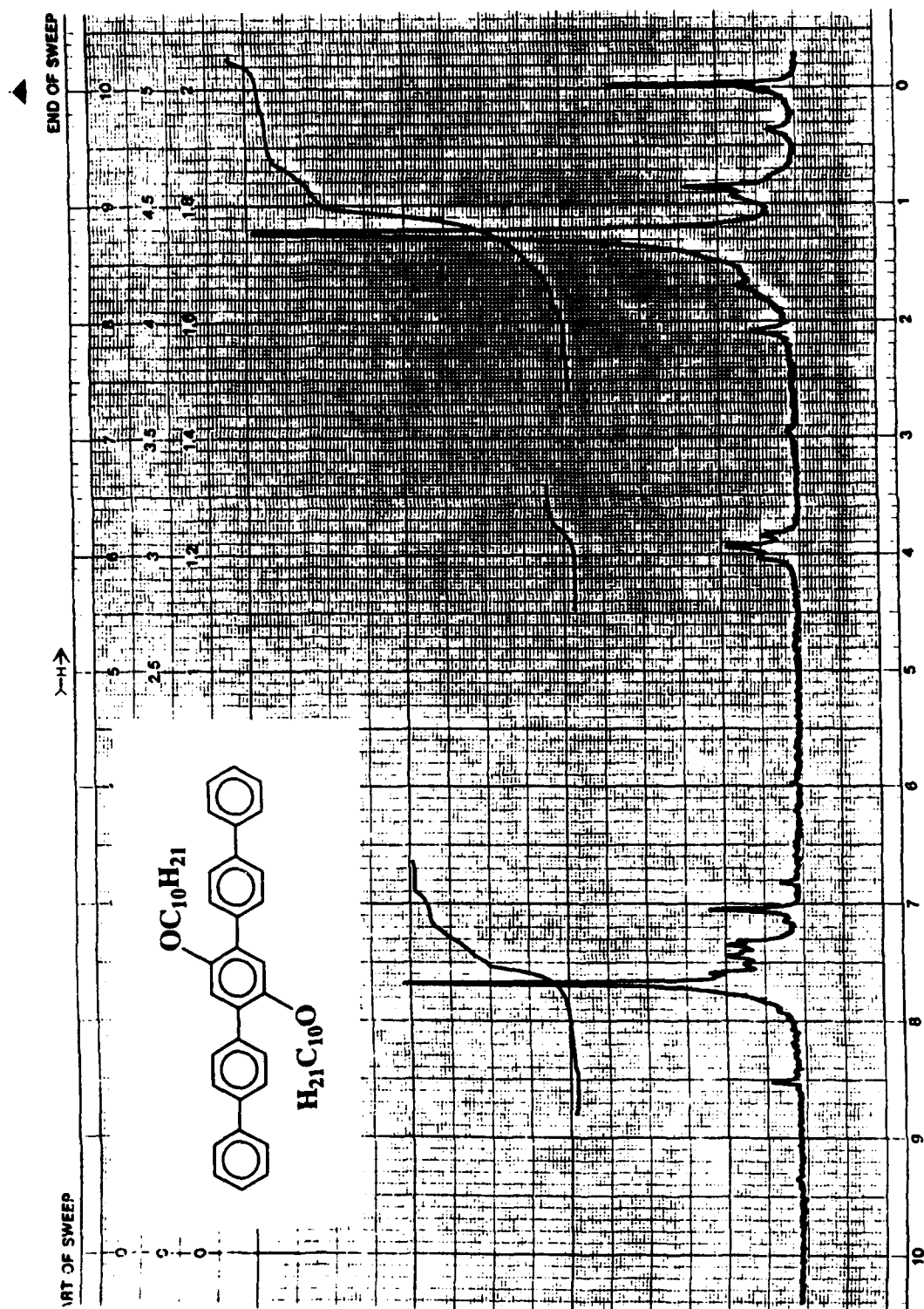
Figure 10. 1H-NMR Spectrum of Didecyloxy Substituted Pentamer.
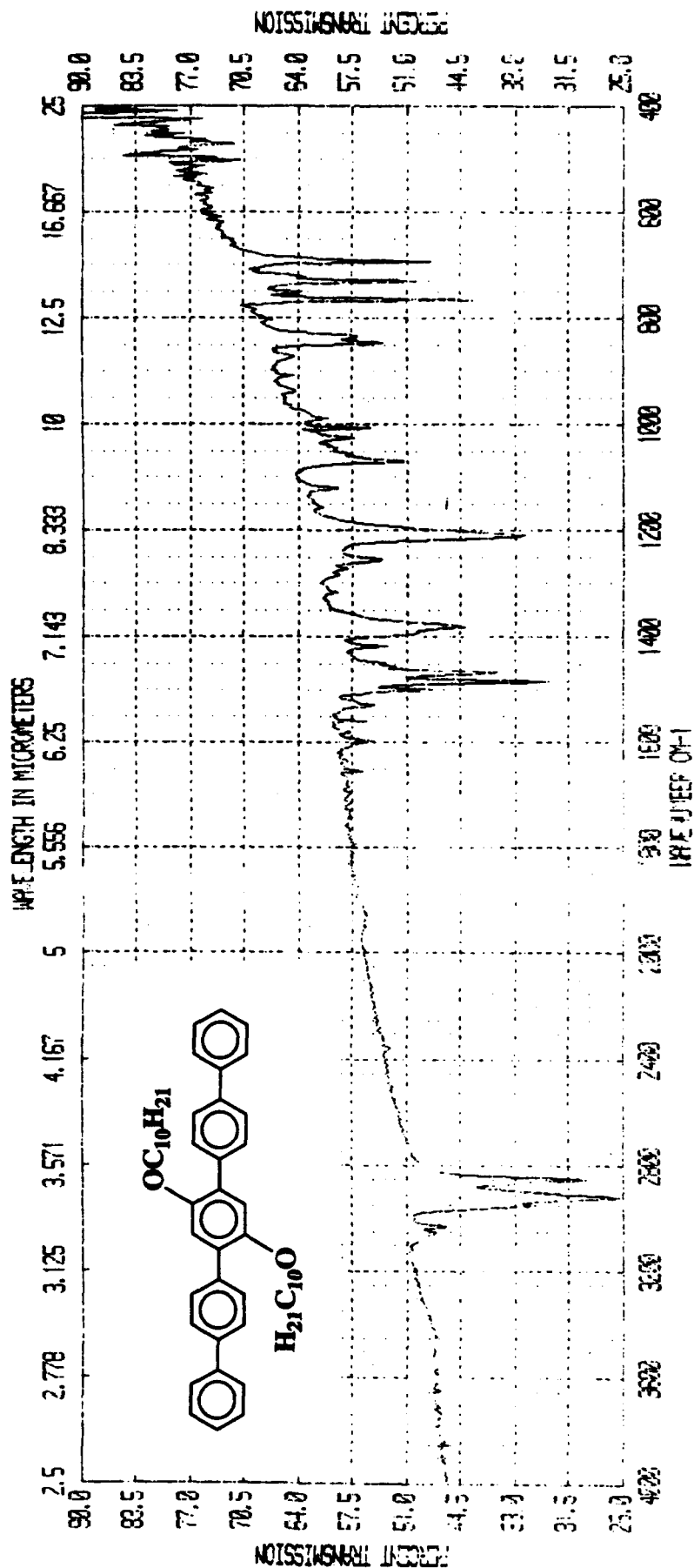
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Figure 11. FTIR Spectrum of Didecyloxy Substituted Pentamer.

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3.1.7. Three-Step Preparation of Heptamer

To a 1000 mL three-necked roundbottom flask fitted with a drying tube and an addition funnel was charged a solution of (*E*)-4-(3-bromo-1-propenyl)biphenyl (10.93 g, 0.040 mol) in chloroform (100mL). A solution of 2,5-didecyloxy-1,4-bis(3-dimethyl-amino-1-propynyl)benzene (11.06 g, 0.020 mol) in chloroform (200 mL) was then added dropwise over a period of an hour to the flask. The solution was allowed to stir under anhydrous conditions for a period of 24 h. The solvent was removed from the reaction mixture *in vacuo* and the solid disalt was suspended into acetone (100 mL) and filtered through a Buchner funnel. After drying the salt in a dessicator overnight, a white powder was afforded (18.24 g, 83%).

The bisammonium bromide intermediate(18.24 g, 0.02 mol) was then transferred to a 500 mL three-necked roundbottom flask fitted with a nitrogen inlet connected to a Firestone valve. Dry toluene (300 mL) was added to dissolve the salt and the solution was stirred under a nitrogen atmosphere for 0.25 h prior to the addition of potassium *t*-butoxide (Aldrich, 3.82 g, 0.03 mol). The solution was allowed to stir for 24 h under a nitrogen atmosphere at which time a TLC (reverse phase; acetone) indicated the reaction was completed. The solution was filtered through a Buchner funnel and the solvent was removed *in vacuo* at room temperature to give a brown residue. The residue was suspended into hexane to precipitate the bisamine intermediate as a white powder which was collected on a medium porosity fritted disc and air dried (6.82 g, 49%).

A solution of the bisamine (5.00 g, 0.01 mol) in 1,2,4-trichlorobenzene (50mL) was stirred in a 100 mL three-necked roundbottom flask fitted with a reflux condenser thermometer, and a nitrogen inlet. The solution was stirred at room temperature for 0.25 h under a nitrogen atmosphere before the flask was slowly raised over a period of 4 h to an internal temperature of 180°C. The solution was stirred under nitrogen atmosphere for a total of 48 h at which time TLC on an alumina gel strip (1:1 hexane:methylene chloride) indicated that the reaction was completed. The reaction mixture was allowed to cool to

room temperature and the precipitate was isolated by filtration over a Buchner funnel (3.34 g). The precipitate was recrystallized from hot cyclohexane (120 mL) to afford a light yellow powder (1.65 g, 36%; 15% overall yield): mp 183-186°C. Elemental analysis and mass spectral data are listed in Table 1. FTIR (KBr): $\nu = 3053$, 3034 (w, arom C-H), 2920, 2854 (s, alkyl C-H), 1484 (s, arom C=C), 1208 (s, assym C-O-C), 1005 cm^{-1} (w, sym C-O-C) (Figure 12).

Figure 12. FTIR Spectrum of Didecyloxy Substiuted Heptamer.

3.2. DFWM Measurements. The system used for measurements of the second hyperpolarizabilities was previously described in another publication (Reference 11). Measurements were carried out on THF solutions of the oligomers using DFWM in a standard time resolved backward beam geometry. The system delivered amplified nearly transform limited 400-femtosecond limited pulses at 602 nm with a repetition frequency of 30 Hz and maximum energy of 0.4 mJ/pulse. Sets of beam splitters and mirrors were used to obtain a series of three synchronous beams that were simultaneously incident upon the sample by delay lines. Peak power at the sample was on the order of 1-20 GW/cm^2. However, one of the synchronous beams was delayed in the backward geometry with respect to the other two beams so that a temporal profile of the DFWM signal was recorded. The signal was observed as the phase conjugate of the probe beam in backward geometry. The signal was monitored with a photodiode and processed with a boxcar averager.

The intensities of the THF solutions of oligomers were compared to a reference sample of THF under similar conditions so that the following equation described the bulk susceptibility of the oligomers:

$$\chi(3) = (n/n_r)^2 \, (I/I_r)^{1/2} \, (l/l_r) \, (\chi_r^{(3)}) \, F \qquad (1)$$

where I stands for the DFWM intensity, n is the refractive index of the medium, l is the interaction length, the subscript r refers to the reference sample and F is the correction factor needed to account for absorption losses. The value of $\chi_r^{(3)}$ for the THF standard has been determined after rigorous comparisons of other reference solvents to be 3.3×10^{-14} esu and is an adopted value for THF at the Photonics Laboratory of SUNY Buffalo. Since the existence of contributions of the solute and solvent to the DFWM measurement contribute to equation (1), the sum of the two contributions may be stated as such:

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$$\chi^{(3)} = L^4(N_S\gamma_S + N_X\gamma_X) \tag{2}$$

where γ_S and γ_X stand for the second hyperpolarizabilities of the solvent and solute respectively, N_S and N_X specify the respective molecular densities, and L is the local field factor in solution which is approximated by using the Lorentz expression. The refractive index, n, in the Lorentz expression was measured using an Abbe refractometer at the sodium line (589 nm). However, this equation only holds true for coherent contributions by both solvent and solute to the real components of the hyperpolarizabilities.

When soluble compounds are measured for their second hyperpolarizabilities, dilute solutions of oligomers at various set concentrations are usually prepared and the $\chi^{(3)}$ values are obtained using equation (1) and then solving equation (2) with a least squares fit to get solute γ values. When no imaginary contribution to $\chi^{(3)}$ is assumed for THF, the following equation must be used:

$$\chi^{(3)}{}_{\text{eff}} = L^4((N_1\gamma_{1r} + N_2\gamma_2)^2 + (N_1\gamma_{1i})^2)^{1/2} \tag{3}$$

where γ_{1r} and γ_{1i} are the real and imaginary components respectively of the second hyperpolarizability of the solute and γ_2 is the second hyperpolarizability of THF. Equation (3) was the preferred equation to determine $\gamma_{(\text{real})}$ and $\gamma_{(\text{im})}$ in this study.

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